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**(54) Title:** METHOD OF INHIBITING RESERVOIR SOURING BY BACTERIA**(57) Abstract**

A method of inhibiting the growth of bacteria, especially anaerobic sulphate reducing bacteria, within oil and gas reservoirs by the addition of peroxy compounds to injected flood water is described. Suitable peroxy compounds include one or more of methyl ethyl ketone peroxyde, cyclohexanone peroxyde, acetyl acetone peroxyde, diacetone alcohol peroxyde, dibenzoyl peroxyde, tertiary butyl peroxyde, tertiary butyl peroxyde, hydrogen peroxyde, tertiary butyl peroxy benzoate, inorganic and organic peroxycarbonates, or functional equivalents or derivatives of these compounds. The peroxy compound additives have the advantage of being thermally sensitive such that penetration into the reservoir and placement in strategic zones can be achieved leading to sterilisation deep within the reservoir. The compounds may also be tailored to optionally scavenge hydrogen sulphide produced by bacterial growth from the reservoir fluids.

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1       **METHOD OF INHIBITING RESERVOIR SOURING BY BACTERIA**

2

3       The present invention relates to a method of reducing  
4       the souring of hydrocarbons due to bacterial production  
5       of hydrogen sulphide gas.

6

7       During the production of hydrocarbon fluids, such as  
8       oil or gas, it is common practice to flood the  
9       reservoir holding the hydrocarbons with water to  
10      enhance production by maintaining pressure as oil  
11      and/or gas is removed and to "sweep" hydrocarbons which  
12      would normally remain within the reservoir to the  
13      collection well.

14

15      The source water used in such flooding operations is  
16      frequently a natural brine and in the case of offshore  
17      oil and gas production is normally sea water.

18

19      Flooding of a reservoir with natural brines usually has  
20      undesirable consequences since the brine may be  
21      responsible for the introduction and/or accelerated  
22      growth of bacteria within a reservoir as follows:

23

24      1.     Bacteria within the brine flood water are  
25      introduced to the reservoir and find a hydrocarbon

1       source (for example, oil). The oil may then be  
2       metabolised by the bacteria allowing the rapid  
3       growth of bacterial populations.

4

5       2. Bacteria which may be naturally present in the  
6       reservoir in dormant form will receive a nutrient  
7       supply due to the introduction of the flood water.  
8       Again, the increased nutrient supply will promote  
9       bacterial growth within the reservoir.

10

11      Generally, anaerobic conditions will exist in the  
12     reservoir, and bacteria able to cope with low amounts  
13     of oxygen or the absence of oxygen will preferentially  
14     proliferate. Generally, the most dominant form of  
15     bacteria is the so called sulphate reducing bacteria  
16     (SRBs). SRBs metabolise sulphates from the injected  
17     flood water and produce hydrogen sulphide gas as a  
18     waste product.

19

20      The hydrogen sulphide generated will become partitioned  
21     in both the oil/gas and water phases within the  
22     reservoir. More importantly, however, the hydrogen  
23     sulphide would normally be co-produced in the fluids at  
24     the producing well.

25

26      The process of hydrogen sulphide production by bacteria  
27     is known as reservoir souring. The consequence of this  
28     process is a gradual increase in hydrogen sulphide  
29     content within the produced fluids.

30

31      Hydrogen sulphide is highly undesirable in the produced  
32     fluids since it is corrosive and toxic. Consequently,  
33     the presence of hydrogen sulphide as a contaminant  
34     adversely affects the sales quality of the exported oil  
35     and gas.

36

1 It is thus normal practice within the industry to  
2 attempt to prevent bacterial growth within the  
3 reservoir by the addition of biocides to the injected  
4 water in order to sterilise the system and therefore  
5 prevent proliferation of bacteria.

6

7 Typical biocides include chlorine, aldehydes such as  
8 gluteraldehyde, thiazolines and quaternary amines.

9

10 However, the continual addition of biocide is  
11 frequently too costly to practice and more usually a  
12 sweep dosage at suitable intervals is used to sterilise  
13 the system.

14

15 Despite biocide addition, it is almost impossible to  
16 prevent the introduction of all bacteria to a reservoir  
17 and a reduced rate of souring may still occur.

18

19 Additionally, due to the surface active nature of the  
20 majority of biocides, the biocides are readily absorbed  
21 to the surfaces of minerals such as clays found in  
22 reservoir sands. It is therefore not normally possible  
23 to achieve penetration of the biocide deep into a  
24 reservoir.

25

26 Hence elimination of bacteria naturally present within  
27 a reservoir or introduced by the flood water and moving  
28 with oil/water flood front boundary is normally not  
29 achievable using conventional biocides.

30

31 One way to obtain an end product having acceptably low  
32 levels of hydrogen sulphide is the removal of that gas  
33 by treating the extracted hydrocarbons. This will  
34 normally require the installation of process equipment  
35 to remove the hydrogen sulphide gas by, for example,  
36 flaring, treating with amine scrubbers to absorb the

1       gas or addition of chemicals to scavenge by reaction to  
2       produce a neutralised compound.

3

4       However, all such methods of hydrogen sulphide removal  
5       considerably increase the cost of production and are  
6       generally considered to be undesirable.

7

8       In summary, it can be seen that a number of options  
9       exist to prevent build up of hydrogen sulphide in the  
10      produced fluids:

11

12      a.     inhibit the growth of bacteria within the  
13           reservoir by chemical addition to the flood water;

14

15      b.     scavenge the evolved hydrogen sulphide within the  
16           reservoir to prevent production with recovered  
17           fluids.

18

19       However, as indicated above, it is apparent that such  
20       treatments are not practical using conventional  
21       biocides or scavengers from performance and/or cost  
22       constraints.

23

24       We have now found that the use of peroxy compounds  
25       (which are not normally thought of as biocides) are  
26       ideally suited to the treatment of bacterially  
27       contaminated reservoirs. The peroxy compounds can both  
28       destroy resident bacteria and also act to remove  
29       hydrogen sulphide already generated.

30

31       In one aspect, the present invention provides a method  
32       of inhibiting the growth of bacteria in a hydrocarbon  
33       reservoir, said method comprising introducing a peroxy  
34       compound to said reservoir.

35

36       In another aspect, the present invention provides a

1 method of combatting the generation of hydrogen  
2 sulphide in a hydrocarbon reservoir by sulphur reducing  
3 bacteria, said method comprising introducing a peroxy  
4 compound to said reservoir.

5

6 The complementary actions of the peroxy compounds arise  
7 from the oxidising potential of such compounds and the  
8 generation of free radicals as the peroxy compound  
9 decomposes.

10

11 The peroxy compounds for use in the present invention  
12 are normally stable neutral compounds which therefore  
13 show minimal absorption to the reservoir minerals and  
14 can therefore penetrate deep into the reservoir carried  
15 by the flood water.

16

17 The peroxy compounds of interest may be selected to  
18 decompose at the particular temperatures encountered  
19 within the reservoir (usually elevated temperatures  
20 relative to the ambient). Particular activation  
21 temperatures can be engineered by selection and/or  
22 modifications of the peroxy compounds used, to allow  
23 the selective placement of compounds within reservoirs  
24 of widely differing temperatures.

25

26 Decomposition of the peroxy compounds leads to the  
27 generation of free radicals which are highly aggressive  
28 towards living cells. The free radicals cause damage  
29 and ultimately destroy cells such as bacteria.

30

31 In addition, the generation of coincident oxidising  
32 species occurs and these oxidising species will react  
33 with hydrogen sulphide leading ultimately to formation  
34 of harmless sulphates in the produced fluids.

35

36 The peroxy compounds therefore have the advantages of

1 being selective to the destruction of bacteria without  
2 being lost to the reservoir by absorption or  
3 decomposition prior to deep penetration. The peroxy  
4 compounds also remove encountered hydrogen sulphide to  
5 prevent continued production within the recovered  
6 fluids.

7

8 The type of peroxy compounds useful for this invention  
9 contain the chemical grouping -O-O- and may be  
10 generally described by the formula:

11



13

14 where R and R' may be hydrogen, alkyl or aromatic  
15 groups (including substituted cyclic and branched  
16 groups), oxygenated hydrocarbon chains such as  
17 carbonate or ketone, or other groups which will result  
18 in stabilisation of the peroxide linkage.

19

20 Modifications to the structure of R and R' alter the  
21 solubility characteristics and thermal stabilities of  
22 the peroxides which allows for selective placement and  
23 activation in reservoirs of differing temperatures and  
24 can also allow penetration of oil layers by selection  
25 of oleophilic peroxides should this be desirable.

26

27 The reaction occurring by thermal decomposition of the  
28 peroxy compounds leads to the generation of free  
29 radicals, thus:

30



31

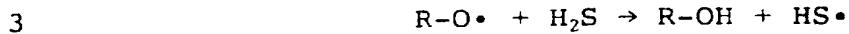


32

33 The generated free radicals may undergo various  
34 reactions leading to complex organic products but all  
35 such reactions lead to cellular attack and therefore  
36 have biocidal properties.

1       In addition, the reaction:

2



4

5       can take place to give a reactive thiol free radical  
6       (HS•) which will bind to organic materials such as  
7       crude oil or bacterial cells to eliminate free H<sub>2</sub>S from  
8       the system.

9

10      A further decomposition reaction can lead to the  
11     formation of free oxygen which again limits bacterial  
12     activity by altering the oxygen free conditions  
13     necessary for SRB growth.

14

15      The described peroxy compounds therefore provide  
16     advantageous multifunctional behaviour which can  
17     prevent reservoir souring.

18

19      Viewed from a further aspect, the present invention  
20     provides the use of a peroxy compound to inhibit  
21     bacterial growth within a hydrocarbon reservoir or  
22     to reduce the hydrogen sulphide content of a  
23     hydrocarbon fluid.

24

25      In addition, the present invention also provides a  
26     hydrocarbon fluid (eg oil or gas) containing a peroxy  
27     compound or a reactant thereof as an additive.

28

29      The range of useful peroxy compounds to be applied to a  
30     reservoir may be characterised by a self accelerating  
31     decomposition temperature (SADT) where a critical value  
32     will cause the compound to decompose at an accelerating  
33     rate yielding the free radicals necessary for biocidal  
34     activity.

35

36      However, the value may be adjusted by the inclusion of

1      accelerators or inhibitors which allow a peroxy  
2      compound to be utilised at temperatures above or below  
3      this figure.

4

5      Examples of suitable peroxy compounds which may be  
6      added to a reservoir flood water for the purpose of the  
7      invention include, but are not limited to:

8

9      Methyl ethyl ketone peroxide,

10     Cyclohexanone peroxide,

11     Acetyl acetone peroxide,

12     Diacetone alcohol peroxide,

13     Dibenzoyl peroxide,

14     Ditertiary butyl peroxide,

15     Tertiary butyl peroxide,

16     Hydrogen peroxide,

17     Tertiary butyl peroxy benzoate,

18     Inorganic and organic peroxycarbonates, or

19

20     functional equivalents or derivatives of these  
21     compounds. A mixture of such compounds may be used.

22

23     Other compounds which are known to generate oxidative  
24     free radicals by thermal or catalytic decomposition  
25     will show similar biocidal activity.

26

27     Generally, the peroxy compounds will be added to the  
28     flood water prior to injection into the reservoir.

## 1        CLAIMS

2

3        1. A method of inhibiting the growth of bacteria in a  
4              hydrocarbon reservoir, said method comprising  
5              introducing a peroxy compound to said reservoir.

6

7        2. A method of combatting the generation of hydrogen  
8              sulphide in a hydrocarbon reservoir by sulphur  
9              reducing bacteria, said method comprising  
10             introducing a peroxy compound to said reservoir.

11

12        3. A method as claimed in either one of Claims 1 and  
13             wherein the peroxy compound may consist of a  
14             water soluble or water dispersable inorganic or  
15             organic based peroxy compound.

16

17        4. A method as claimed in any one of Claims 1 to 3,  
18             wherein the peroxy compound may be a peroxide,  
19             hydroperoxide, peroxy carbonate, peroxy sulphate or  
20             other peroxide based complex.

21

22        5. A method as claimed in any one of Claims 1 to 4,  
23             wherein the peroxy compound may be selected from  
24             one or more of methyl ethyl ketone peroxide,  
25             cyclohexanone peroxide, acetyl acetone peroxide,  
26             diacetone alcohol peroxide, dibenzoyl peroxide,  
27             ditertiary butyl peroxide, tertiary butyl  
28             peroxide, hydrogen peroxide, tertiary butyl peroxy  
29             benzoate, inorganic and organic peroxy carbonates,  
30             or functional equivalents or derivatives of these  
31             compounds.

32

33        6. A method as claimed in any one of Claims 1 to 5,  
34             wherein said peroxy compound is added to the  
35             reservoir flood water.

36

10

- 1       7. A method as claimed in any one of Claims 1 to 6,  
2       wherein the peroxy compound is selected to  
3       decompose at a temperature of the reservoir.
- 4
- 5       8. A method as claimed in any one of Claims 1 to 7,  
6       wherein a co-additive may be optionally added to  
7       the peroxy compound to either inhibit or  
8       accelerate decomposition of the peroxy compound as  
9       a function of temperature.
- 10
- 11      9. Use of a peroxy compound to inhibit bacterial  
12       growth within a hydrocarbon reservoir.
- 13
- 14      10. Use of a peroxy compound to reduce the hydrogen  
15       sulphide content of a hydrocarbon fluid.
- 16
- 17      11. Hydrocarbon fluid containing a peroxy compound or  
18       a reactant thereof as an additive.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/GB 97/01537

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C10G 27/12, A01N 37/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C10G, A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, APIPAT

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AU 53138/79 A1 (BIOLEX CORP.), 28 May 1981 (28.05.81), page 6, line 35 - page 8, line 1 - line 16, claims 1-7  --	1-11
A	EP 0082513 A1 (PEROXID-CHEMIE GMBH), 29 June 1983 (29.06.83)  -----	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

06/08/97

International application No.  
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
AU 53138/79 A1	28/05/81	NONE		
EP 0082513 A1	29/06/83	CA 1205616 A DE 3151133 A US 4548708 A		10/06/86 30/06/83 22/10/85